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DEVIATIONS FROM MATTHIESSEN'S RULE  
IN ALUMINUM - MAGNESIUM ALLOYS

by

RAJINDER S. SETH

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
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UNIVERSITY OF ALBERTA  
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read,  
and recommend to the Faculty of Graduate Studies for  
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RULE IN ALUMINUM - MAGNESIUM ALLOYS submitted by Rajinder S. Seth  
in partial fulfilment of the requirements for the degree of  
Master of Science.



## ABSTRACT

The deviations from Matthiessen's rule in alloys of aluminum with magnesium impurity over the temperature range from  $4.2^{\circ}\text{K}$  to  $300^{\circ}\text{K}$  have been measured. The deviations are found to be positive throughout the temperature range and have complicated behaviour. At high temperatures, the deviations have a positive temperature-variation. The deviation versus temperature curves for a pair of alloys, in which the solute and the solvent atoms exchange roles, are expected to have opposite slopes at high temperatures. In view of this, comparison has been carried out with the reported measurements of deviations over the temperature range from  $4.2^{\circ}\text{K}$  to  $373^{\circ}\text{K}$  in alloys of magnesium with aluminum impurity, wherein, a negative temperature-variation of deviations above  $70^{\circ}\text{K}$  has been observed. Thus the expected behaviour is verified for the aluminum-magnesium system.





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## INTRODUCTION

The characteristic property of a metal is its large electrical conductivity and therefore its study is of fundamental importance in understanding the transport phenomena in solids. The addition of a small amount of impurity atoms into the metallic lattice, in general, modifies the transport properties considerably and, in particular, enhances the electrical resistivity of the metal. It was realized as early as 1864 that the electrical resistivity of a relatively pure metal could be written as the sum of a temperature-dependent part, characteristic of the host metal, and a temperature-independent part which depends on the amount and nature of the impurities present. This is known as Matthiessen's rule and is nearly true for all metals.

From the theoretical point of view, the problem of electrical resistivity itself is quite complicated and not completely understood. On the basis of certain simplifying assumptions, theoretical justification for Matthiessen's rule has been given. On the other hand, departures from it are expected and have been measured in various dilute alloys. The study of these departures and the various factors on which they depend is a problem of considerable interest to both the theoretical and the experimental physicist.



This thesis reports the measurements of deviations from Matthiessen's rule in two dilute alloys of aluminum and magnesium over the temperature range from  $4.2^{\circ}\text{K}$  to  $300^{\circ}\text{K}$ .

Our interest in the problem began with a suggestion by Professor A. B. Bhatia to look for the temperature dependence of deviations in alloys in which the solvent and the solute metals exchange roles, that is, in complementary alloy pairs. At high temperatures, the deviation vs. temperature curves for the two alloys are expected to have opposite slopes (Appendix 1). Krautz and Schultz (1957) have studied a pair of gold and silver alloys ( $\text{Au} + 1$  atomic percent Ag and  $\text{Ag} + 0.6$  atomic percent Au) over the temperature range from  $10^{\circ}\text{K}$  to  $300^{\circ}\text{K}$  but their results do not indicate the reversal of slope. Hedgcock and Muir (1964) in a study of alloys of magnesium measured deviations from Matthiessen's rule for magnesium-aluminum\* alloys with 0.29, 0.80 and 2.41 at. % nominal Al content. Their measurements for the latter alloy show positive deviations above  $30^{\circ}\text{K}$ , increasing with temperature up to about  $70^{\circ}\text{K}$ . Above this temperature the deviations decrease almost linearly with temperature, becoming negative around  $120^{\circ}\text{K}$ . We chose the

---

\* The abbreviations Al and Mg will be used for aluminum and magnesium respectively and the notation "at. % Mg" or simply "% Mg" will be used in place of atomic percent magnesium for convenience in referring to the specific alloys.





aluminum - magnesium system and have completed measurements on two alloys of Al with 2.0 at. % and 1.5 at. % nominal Mg content.

Unfortunately, owing to the lack of experimental data on the impurity resistivity of alloys and to the absence of a satisfactory theory, the problem of deviations from Matthiessen's rule is not properly understood. A recent attempt in this direction has been made by Kagan and Zhernov (1966) and their theory does give a reasonable qualitative agreement with some of the existing experimental data.

This thesis is divided into three parts. In the first part, a brief survey of the existing theories and some of the published experimental work is given. A brief description of the theory of Kagan and Zhernov (1966) completes this section. In the second part, the apparatus, preparation of the alloys and the experimental technique for the measurement of deviations is described. In the third part the experimental results are presented and discussed, and a possible explanation is given in the light of Kagan and Zhernov's theory.



## PART I

### THEORY

#### 1.1 General

The resistivity of a metal may be considered to arise from two main contributions: (a) the 'ideal' resistivity,  $\rho_i$ , due to the scattering of electrons by the thermal vibrations of the lattice, which one expects to be temperature-dependent, and (b) the resistivity,  $\rho_o$ , due to static lattice defects such as impurity atoms, vacancies, and dislocations which one would not expect to be dependent on the temperature. This separation of the resistivity into two components is to a fair approximation, well justified and is known as Matthiessen's rule (1864) which may be written in the form,

$$\rho(T) = \rho_i(T) + \rho_o. \quad (1)$$

Figure 1 shows the type of behaviour for the variation of resistivity with temperature.  $\rho_o$  remains constant whereas  $\rho_i$  decreases to zero at  $0^\circ \text{K}$ . The total resistivity (according to Matthiessen's rule) shown by the broken line will thus decrease as temperature is reduced, but it will attain a constant value  $\rho_o$  at very low temperatures. For this reason  $\rho_o$  is called the residual resistivity and its value will depend on the physical and chemical purity of the metal.





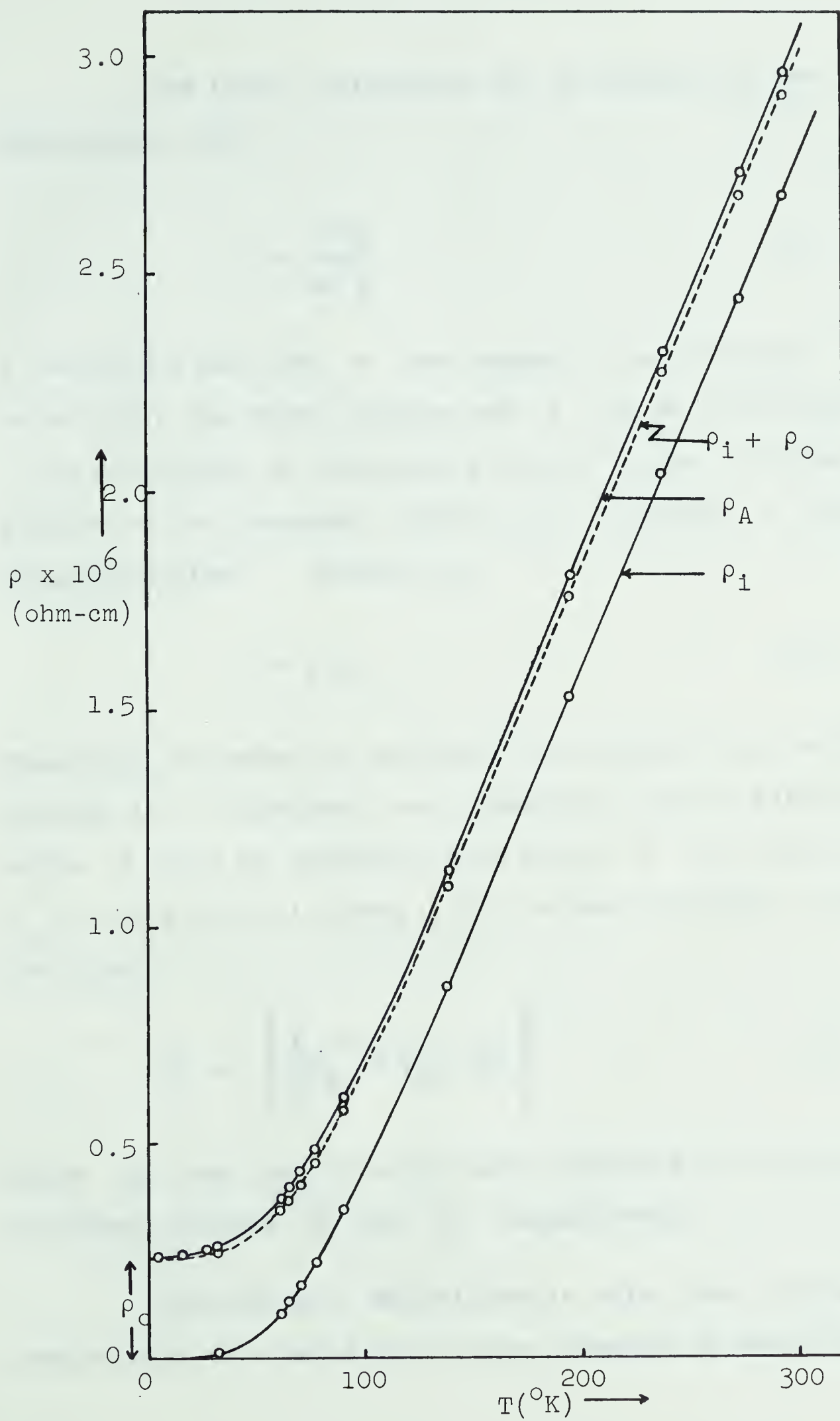
Figure 1

(Matthiessen's Rule)

Graph showing the temperature - variation of

- (i) the ideal resistivity,  $\rho_i$ , of aluminum,
- (ii) sum of  $\rho_i$  and the residual resistivity,  $\rho_o$ , of the Al + 2 % Mg alloy,
- (iii)  $\rho_A$ , the measured resistivity of the Al + 2% Mg alloy.







The ideal resistivity can be written in the form  
(Rosenberg, 1963)

$$\rho_i = \frac{mv_F}{ne^2\ell} \quad , \quad (2)$$

$m$  being the mass and  $e$  the charge of the electron,  $v_F$  its velocity at the Fermi surface and  $\ell$  its mean free path;  $n$  is the number of electrons per unit volume. The main problem of the transport theory is to calculate  $\ell$  or the relaxation time  $\tau$  defined by

$$\ell = \tau v_F \quad . \quad (3)$$

Therefore, in order to calculate the resistivity, the main problem is to calculate the probability that an electron in state  $\vec{k}$  will be scattered into state  $\vec{k}'$  by a perturbation  $U$  in the potential energy.  $1/\tau$  always contains a term of the form

$$\frac{1}{\tau} \propto \left| \int \psi_{\vec{k}}^* U \psi_{\vec{k}'} d\vec{k}' \right|^2 \quad , \quad (4)$$

where  $\psi_{\vec{k}}$  and  $\psi_{\vec{k}'}$  are the wave functions of the electron with wave vectors  $\vec{k}$  and  $\vec{k}'$  respectively.

According to Matthiessen's rule, the increase in resistivity of a metal due to the presence of small amount of





impurity in solid solution is independent of temperature. The impurity atoms disturb the periodicity of the field within the lattice and electrons will be scattered by these atoms and a resistance will arise even in the absence of any thermal agitation. If  $1/\tau_o$  be the number of times per second that an electron is scattered by an impurity atom and  $1/\tau_t$  the number of times that it is deflected owing to the thermal vibrations of the atoms, then assuming that the effects of impurity atoms and thermal agitation are additive, we can write

$$\frac{1}{\tau} = \frac{1}{\tau_o} + \frac{1}{\tau_t} \quad . \quad (5)$$

It follows that

$$\rho = \rho_o + \rho_t \quad ,$$

where  $\rho_o$  is the residual resistivity of the alloy and is independent of temperature;  $\rho_t$  will be approximately proportional to the temperature, as for a pure metal (Mott and Jones, 1936).

Matthiessen's rule is satisfied if:

1. The effective number of free electrons is unaltered by the addition of foreign atoms,



2. The thermal vibrations of impurity atoms give the same scattering as those of the atoms of the solvent metal. Neither of these conditions is fulfilled exactly. The presence of an impurity atom in the crystal lattice makes itself felt in one or more of the following ways:

- (a) If the charge on the impurity atom is different from that of the solvent atoms, then the potential around it will also be different and so it will scatter electrons.
- (b) The impurity atoms might change the number of conduction electrons and hence the position of the Fermi surface in the Brillouin zone might be altered.
- (c) The impurity atoms might themselves affect the dimensions and geometry of the Brillouin zones.
- (d) Over - or - undersized impurity atoms will distort the lattice thereby upsetting the periodicity of the lattice.

## 1.2 Deviations from Matthiessen's Rule

According to Sondheimer (1950) departures from Matthiessen's rule can be expected and are significant when the ideal resistivity and the residual resistivity are of the same order of magnitude. His calculations based on the solution of the Boltzmann transport equation using a variational method and assuming the free electron model show that the deviations are positive, depend on temperature and concentration





of the solute but are much too small ( $\sim 1\%$  of total resistivity) to agree with experiment. Also departures are expected (Sondheimer and Wilson, 1947; Kohler, 1949) and indeed found (Krautz and Schultz 1954; Alley and Serin, 1959; Das and Gerritsen, 1964; Hedgcock and Muir, 1964) in multivalent metals, which may be described by a two-band model (Sondheimer and Wilson, 1947). It is demonstrated that if the electrons in each conduction band behave independently, Matthiessen's rule applies separately to each band. However, deviations occur when the total conductivity, which is the sum of the conductivities of the two bands, is evaluated. Accordingly, it turns out that the deviations  $\Delta\rho$  are positive and strongly temperature-dependent. At low temperatures where  $\rho_0 \gg \rho_i$ ,  $\Delta\rho \propto \rho_i$  but independent of  $\rho_0$ . At high temperatures where  $\rho_i \gg \rho_0$ ,  $\Delta\rho \propto \rho_0$  and independent of  $\rho_i$ . It is therefore seen that  $\Delta\rho = 0$  when  $T = 0$ ; it increases as  $T$  increases and finally reaches a constant value proportional to  $\rho_0$ . Experimental studies of Matthiessen's rule in dilute alloys often indicate a more complicated behaviour than can be accounted for by the above theory.

In the earlier analyses of this problem, the impurity atoms were regarded as static. This led to the temperature-independent residual resistivity in Matthiessen's rule. Actually, the impurity atoms oscillate and the character of their



oscillations may differ greatly from the oscillations of the atoms of the host lattice. The electrons will thus experience additional inelastic scattering not only from the impurity atom itself, but also from a noticeable number of atoms that surround the impurity atom and whose oscillations are perturbed.

Koshino (1960) proposed that the scattering of electrons by the thermal motion of the impurities in monovalent metals could lead to a significant additional resistivity proportional to temperature  $T$  in the high-temperature limit and to  $T^2$  in the low-temperature limit. His result was later criticized by Taylor (1962) on the grounds that in an expansion of lattice displacements, he had omitted a set of terms which give a contribution almost exactly cancelling the rest of the series. A rigorous demonstration was given that when the change in electron energy is neglected, the scattering of a single free electron by an impurity atom is quite independent of its thermal motion. No attempt was made to solve the Boltzmann equation using this revised expression for the scattering, and only an intuitive argument was given that the presence of other electrons would not modify the scattering enough to cause any appreciable change in resistivity. However, further work by Klemens (1963) and Koshino (1963) questioned this view which led Taylor (1964) to derive



an explicit expression for the scattering probability and show that the solution of the Boltzmann equation resulted in a negligible change in resistivity.

While Koshino (1960) considered that the phonon-assisted impurity scattering arises from the displacement of the impurity potential due to the thermal motion of impurity and assumed that the charge cloud was rigid around the impurity, the lattice vibrations produce thermal strain around the impurity ion. This strain induces charge redistribution and leads to the distortion of the impurity potential modulated by the time-varying strain field of a lattice wave. The distortion of the impurity potential was first treated by Klemens (1963). If the fractional change of the impurity potential due to a strain  $\epsilon$  is  $A^{\frac{1}{2}}\epsilon$ , then the deviation from Matthiessen's rule due to these additional processes is given by

$$\Delta\rho(T) = A \rho_0 \langle \epsilon^2 \rangle, \quad (1)$$

where  $\rho_0$  is the residual resistivity,  $A$  is a numerical constant, and  $\langle \epsilon^2 \rangle$  is the mean-square thermal strain at the impurity site. If the mechanical properties of the impurity cell are the same as for a cell of a perfect crystal,  $\langle \epsilon^2 \rangle$  is proportional to the vibrational energy of the crystal, so that  $\Delta\rho(T) \propto T^4$  at low temperatures and  $T$  at high temperatures.





Deviations proportional to  $T$  have been observed at ordinary temperatures in many systems (Gerritsen, 1956) and deviations proportional to  $T^4$  have been observed at liquid-hydrogen temperatures in Au-Pt and Au-Cu alloys (Damon and Klemens, 1964) and Ag-In alloys (Damon and Klemens, 1965).

Klemens (1963) also pointed out that if phonon-assisted scattering makes an appreciable contribution to the resistivity of an alloy, then any peculiarity in the temperature dependence of the mean-square thermal strain at impurity site should be reflected in the electrical resistivity. In particular, if the impurity atoms are considerably lighter than the solvent atoms, so that there are localized modes about these impurities with a frequency well above the continuum of acoustic modes, then a substantial fraction of the deviation from Matthiessen's rule should reflect the temperature dependence of the energy of the local modes. In order to test this supposition, Damon and Klemens (1965) measured deviations for 5 gold alloys with 1 and 1.6 at. % platinum, 1.8 at. % zinc, 2.4 at. % aluminum and 2.6 at. % copper in the temperature range from 80°K to 500°K. It had been expected that the local modes would cause a small but observable increase with temperature of the slope of the resistivity versus temperature curve around  $\theta_0/2$  where  $\theta_0$  is the characteristic temperature of the local mode.



However, substantial deviations from Matthiessen's rule were found but not the temperature-variation expected from local modes. It was suggested that this effect could have been obscured by deviations from Matthiessen's rule arising from the zone structure of gold.

### 1.3 Theory of Kagan and Zhernov (1966)

The basic premises of this theory are the following:

- (a) The free electron approximation is used and variation of the electron spectrum due to introduction of impurity is neglected.
  - (b) The "rigid ion" model is used for the electron-ion interaction and analysed by Born approximation.
  - (c) The alloy is considered to be a dilute substitutional solid solution and therefore variation of the force constants in the dynamic matrix of oscillations is neglected.
  - (d) The lattice is assumed to be cubic and monatomic.
- Almost all these assumptions are not critical and do not change the qualitative picture.

Within the framework of these assumptions, the probability  $W_{\vec{k}\vec{k}'}$  that scattering causes transition of electron from a state with wave-vector  $\vec{k}$  and energy  $\epsilon_{\vec{k}}$



to a state with wave-vector  $\vec{k}'$  and energy  $\epsilon_{\vec{k}'}$  is written in the form

$$W_{\vec{k}\vec{k}'} = W_{\vec{k}\vec{k}'}^{\text{ideal}}(\vec{q}, w) + W_{\vec{k}\vec{k}'}^{\text{impurity}}(\vec{q}, w), \quad (1)$$

where

$$\vec{q} = \vec{k} - \vec{k}' \quad \text{and} \quad \hbar w = \epsilon_{\vec{k}} - \epsilon_{\vec{k}'}, \quad .$$

$W_{\vec{k}\vec{k}'}^{\text{ideal}}$  is the probability of single-phonon scattering of the electrons in an ideal crystal and therefore determines the resistivity of an ideal lattice.  $W_{\vec{k}\vec{k}'}^{\text{impurity}}$  determines the probability of the electron scattering due entirely to the presence of impurity atoms. It takes into account the elastic scattering by impurities which gives rise to residual resistivity. Also it takes into account the inelastic scattering due to,

- (i) the deformed phonon spectrum of the lattice,
- (ii) direct scattering by the oscillating impurity atoms, and
- (iii) the interference between the scattering by impurity ion and the perturbed phonon spectrum. The expression for the resistivity is written as

$$\rho = \rho(\text{Ideal}) + \rho(\text{Impurity}),$$

and

(2)

$$\rho(\text{Impurity}) = \rho_0 + \Delta\rho .$$





As  $T \rightarrow 0$ ,  $\Delta\rho \rightarrow 0$  and only  $\rho_0$ , the residual resistivity, which is the part due to elastic scattering, remains.

In the region of low temperatures,  $\frac{\Theta}{T} \gg 1$  where  $\Theta$  is the characteristic Debye temperature, the ideal resistivity is given by the well-known Bloch-Grüneisen formula and varies as

$$\rho_{\text{ideal}} \propto T^5/\Theta^6. \quad (3)$$

For the impurity part of the resistivity, it is shown that the electron scattering by an oscillating impurity ion leads to the appearance of a term proportional to  $T^2$ , interference between scattering by an impurity ion and by a perturbed phonon spectrum to a term proportional to  $T^4$ , and scattering by a deformed phonon spectrum to a term proportional to  $T^5$ . For low impurity concentrations, all these terms are proportional to the concentration. The total contribution of all these terms is written approximately as

$$\rho(\text{Impurity}) \simeq A T^2/\Theta^3 + BS T^5/\Theta^6, \quad (4)$$

where the quantity  $S$  is given by

$$S = \frac{M' - M}{M} + \frac{Z' - Z}{Z}. \quad (5)$$

$M$  and  $M'$  denote respectively the mass of the host atom and the mass of the impurity atom in the lattice and  $Z$  and  $Z'$



denote the respective charges on the host ion and the impurity ion in the matrix.  $A$  and  $B$  are positive constants.

The first term in equation (4) is always positive and the sign of the second term is determined by the sign of the quantity  $S$ . If  $S < 0$ , it is shown that the impurity resistivity as a function of temperature passes through a maximum given by

$$(\rho_{\text{impurity}})_{T_{\text{max}}} = 3 C (-S) (\rho_{\text{ideal}})_{T_{\text{max}}}, \quad (6)$$

where  $C$  is the concentration of the impurity atoms.

When  $S > 0$ , the impurity resistivity is expected to increase monotonically with the temperature.

The further temperature-variation of impurity resistivity is expected to exhibit a number of anomalies, especially in the case of heavy impurity atoms. At high temperatures, it is shown that the impurity part of the resistivity varies linearly with temperature, the sign of the derivative being positive or negative depending on the relative positions of the impurity and host atoms in the periodic table.

It is also pointed out that the deformation of the electron spectrum can in some cases complicate the result.



## PART II

### EXPERIMENTAL WORK

#### II.1 General

The experimental determination of the deviations from Matthiessen's rule over the temperature range  $4.2^{\circ}\text{K} \leq T \leq 300^{\circ}\text{K}$  poses problems which are not normally encountered in the measurement of electrical resistivity over the same temperature range.

Before indicating in detail how these problems have been met, it is perhaps desirable to first mention what the problems are. Let us consider the measurement of  $\rho(T)$ . Assuming that Matthiessen's rule is obeyed, one has

$$\rho(T) = \rho_0 + \rho_i(T) \quad , \quad (1)$$

where the residual resistivity  $\rho_0$  is given the operational definition

$$\rho_0 = \lim_{T \rightarrow 0} \rho(T) \quad .$$

The measured quantity is the resistance  $R(T) = \rho(T) f$ , where  $f$  is a geometrical factor which depends on the shape of the specimen. For a straight uniform wire of length  $\ell$  between potential contacts and area of





cross-section  $A$ ,  $f = \frac{\ell}{A}$ . Since  $f$  has the dimensions of  $L^{-1}$ , it is temperature-dependent due to the thermal expansion of the wire. For Al the effect of thermal expansion on  $\frac{\ell}{A}$  is only about 0.4 % between 4.2°K and room-temperature. However, it is usually ignored\*. Equation (1) may therefore be written as

$$\frac{\rho_i(T)}{\rho_i(273)} = \frac{\rho(T) - \rho_o}{\rho(273) - \rho_o} = \frac{R(T) - R_o}{R(273) - R_o}, \quad (2)$$

so that measuring the resistance only of a wire sample over a range of temperatures including the ice-point is sufficient to determine the normalized ideal resistivity

$$\frac{\rho_i(T)}{\rho_i(273)}.$$

Let us now consider the case where Matthiessen's rule is not obeyed. One has

$$\rho(T) = \rho_i(T) + \rho_o + \Delta\rho(T), \quad (3)$$

where  $\rho_o = \lim_{T \rightarrow 0} \rho(T)$  and  $\rho_i(T) = \lim_{\rho_o \rightarrow 0} \rho(T)$ .

---

\* It may be mentioned here that accurate enough data on thermal expansion of various metals and alloys seldom exist to make meaningful corrections.



The only "a priori" assumption which may be made about  $\Delta\rho$  is that  $\Delta\rho(0) = 0$ . One also expects  $\Delta\rho(T)$  to be small compared to  $\rho_i(T)$  or  $\rho_0$  in order for Matthiessen's rule to have originated in the first place. The net result is that if  $\Delta\rho$  is to be measured at high temperatures ( $T \simeq \Theta$ ), the geometrical factor  $f$  must be determined for the sample and furthermore,  $f$ ,  $R_0$  and  $R(T)$  must be measured accurately if even a modest accuracy is to be obtained for  $\Delta\rho$ . This last result is obtained simply because large measured quantities are subtracted to get relatively small quantity  $\Delta\rho$ .

It is possible to obtain useful information about  $\Delta\rho$  at low temperatures ( $0 \leq T \leq 40^\circ\text{K}$ ) without measuring  $f$  through the use of normalization (Berry, 1963) but these techniques cannot be extended to higher temperatures without making further assumptions about  $\Delta\rho$  at these temperatures (Alley and Serin, 1959).

The accuracy required for  $\rho_i(T)$  exceeds the accuracy of the published values at least for Al, so that it was necessary to make simultaneous measurements on a relatively pure sample and an alloy sample. In this way, it was only necessary that the two samples were at the same temperature for any given measurement, and the temperature itself was only required to an accuracy commensurate with the final accuracy of  $\Delta\rho$ .



To meet these requirements, it was necessary to (a) modify an existing cryostat so that two wire samples could be maintained at the same temperature through the use of exchange gas, (b) put into operation a new potentiometer with the required linearity, stability, thermal emf rejection, and voltage sensitivity, and (c) construct a potential distribution measuring device to ensure that effects due to non-uniform cross-section of wires and inhomogeneity of composition of alloys were negligible. Considerable care was taken to ensure that the 'pure' wire samples did in fact end up in a reasonably pure state as mounted, and the alloy samples were indeed homogeneous substitutional alloys with the nominal Mg concentration and little other impurity.

These various points are now discussed in detail.

## II.2 The Cryostat

The cryostat used has been described by White and Woods (1955). In addition it has been described in more detail by Adler (1960) and Rogers (1962). For the purpose of the present work, it was modified and rewired.

In this cryostat, which is shown in Figure 2, the specimen chamber was made vacuum tight in order to use exchange gas around the specimen. It could be thermally isolated from



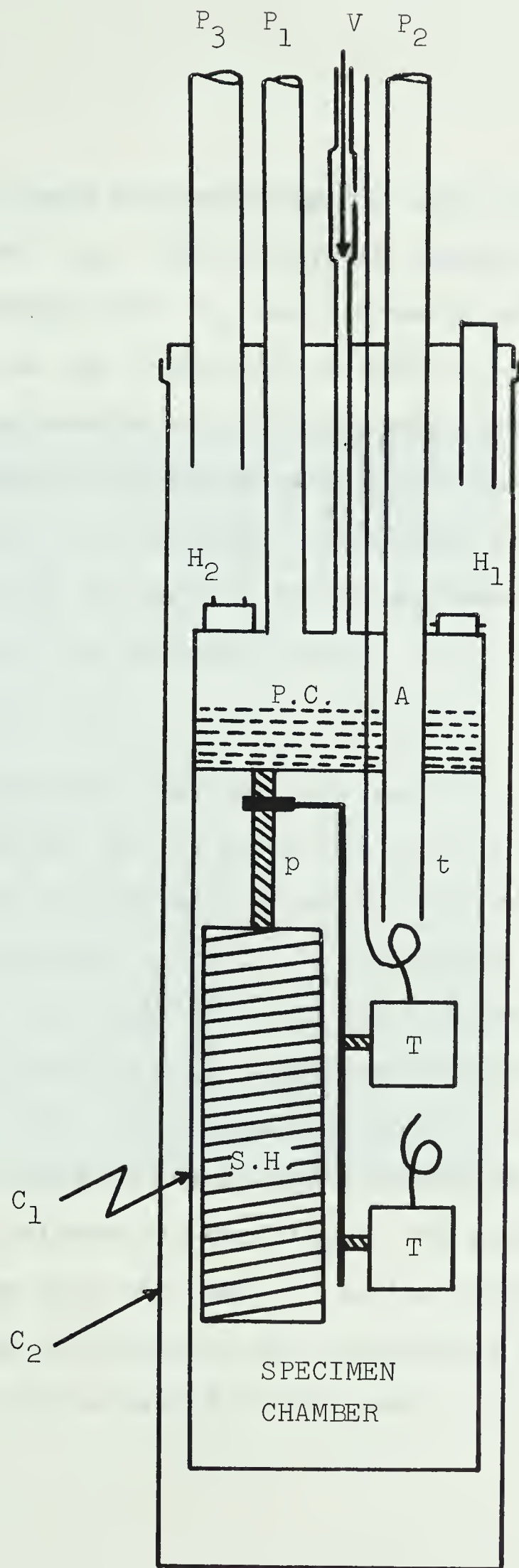


Figure 2

## The Cryostat

$P_1, P_2, P_3$	-	Pumping Tubes
V	-	Needle Valve
$H_1, H_2$	-	Heaters
P.C.	-	Pumping Chamber
t	-	Post for thermal anchoring of leads
T	-	Gas Thermometer Bulbs
$C_1$	-	Inner Can
$C_2$	-	Outer Can
S.H.	-	Specimen Holder
p	-	Post for mounting the specimen holder







the refrigerant bath by evacuating the space between the two cans  $C_1$  and  $C_2$ . The electrical leads were brought in through the pumping tube  $P_2$  and thermally anchored at  $t$  so as to minimize the conduction of heat to the inner chamber. A radiation trap consisting of blackened copper wool placed between two plugs of styrofoam was inserted at  $A$  in the pumping tube  $P_2$ . The specimen chamber was cooled below the temperature of the bath by reducing pressure over the liquid boiling in the pumping chamber P.C. by pumping through the tube  $P_1$ .

In the first run, the specimen wires (one of pure Al and the other of Al + 2 at. % Mg) each of about 0.5 mm diameter and 100 cm long were loosely wound on a cross-shaped lucite specimen holder. In the second run, the specimens (pure Al and Al + 1.5 at. % Mg wires) were wound in a 0.025 inch x 0.025 inch groove milled on a lucite cylinder (Figure 3). Potential contacts in the form of brass clips attached to the specimen holder were used and the leads were soldered to the clips. The specimen holder could be slipped onto the post  $p$  in the cryostat. The two bulbs of the differential gas thermometer were tied to a thick copper wire attached to the post  $p$ .





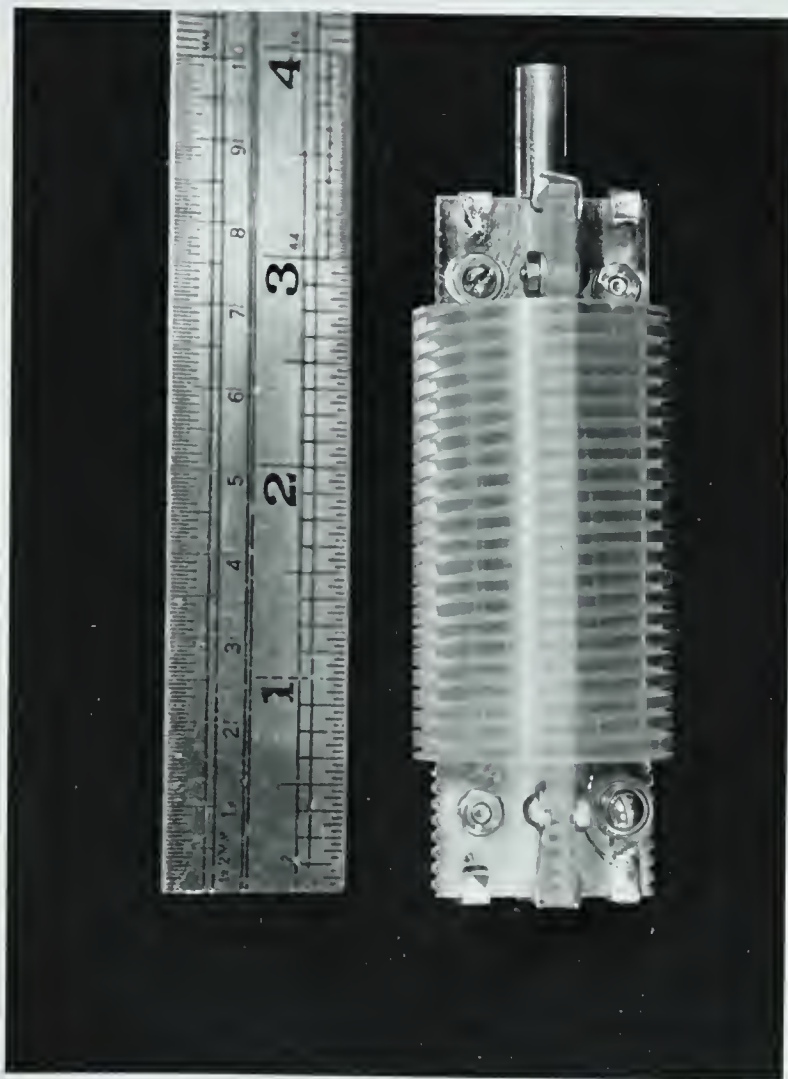


Figure 3

The Specimen Holder



The operation of the cryostat was as follows:

- (a)  $4.2^{\circ}\text{K}$  to  $45^{\circ}\text{K}$ . With liquid helium as the refrigerant, the temperature above  $4.2^{\circ}\text{K}$  was maintained by using the electronic temperature controller (White and Woods, 1955; Dauphinee and Woods, 1955) to heat the inner can with the outer can evacuated to pressure  $\sim 10^{-6}$  mm of mercury.
- (b)  $55^{\circ}\text{K}$  to  $90^{\circ}\text{K}$ . With liquid oxygen around the outer can, the temperature was controlled within  $0.01^{\circ}\text{K}$  by pumping through a Cartesian Manostat (White, 1959) over liquid oxygen in the pumping chamber. To avoid any hazards due to combustion of hydrocarbons, a rotary pump with tricresyl phosphate (T.C.P.) was used. In the range from  $65^{\circ}\text{K}$  to  $78^{\circ}\text{K}$ , liquid nitrogen was also used.
- (c) Above  $90^{\circ}\text{K}$ . With liquid oxygen around the outer can and the space between  $C_1$  and  $C_2$  evacuated to pressure  $10^{-6}$  mm of mercury, the inner can was heated by passing a constant current from the mains through a 500 ohm wire-wound resistor attached by epoxy resin cement to the top of the pumping chamber. Sufficient time was allowed ( $\sim 24$  hours) for thermal equilibrium to be reached in the inner can before each reading.



(d)  $194^{\circ}\text{K}$  and above. Solid carbon dioxide (dry ice) was used as refrigerant. Exchange gas was admitted into both cans for the measurement at  $194^{\circ}\text{K}$ . For temperatures above  $194^{\circ}\text{K}$ , the 500-ohm heater was used with the outer can pumped to  $10^{-5}$  mm pressure.

(e)  $273^{\circ}\text{K}$ . With exchange gas in both cans, the outer can was surrounded by ice flakes in a large covered dewar. Water was continuously siphoned out.

(f) Room Temperature. A thermometer was attached to the tube  $P_2$  and a dewar was put around the outer can. Exchange gas was admitted to both cans. The thermometer could be read through the unsilvered strip in the dewar.

### II.3 Temperature Measurement

Since the temperatures at which  $\Delta\rho(T)$  was determined were not required to a high accuracy, it was possible to use the pure Al sample itself as a resistance thermometer at temperatures above  $40^{\circ}\text{K}$ . At lower temperatures a constant volume gas thermometer (White, 1959) was used. Temperatures in the range  $55^{\circ}\text{K}$  to  $90^{\circ}\text{K}$  were determined from vapour pressure measurements (Linder, 1950). The sublimation temperature of solid  $\text{CO}_2$  was calculated from the relation (Scott, 1959)





$$T(^{\circ}\text{K}) = \frac{1349}{9.81137 - \log_{10} P} \quad ,$$

where  $P$  is the atmospheric pressure in millimeters of mercury. A mercury-in-glass thermometer was adequate for ice-point and higher temperatures.

The boiling temperatures of liquid oxygen and liquid nitrogen obtained from their vapour pressures were checked against another vapour pressure thermometer containing spectroscopically pure oxygen (Rogers, 1962). A close agreement ( $0.03^{\circ}\text{K}$ ) was found.

#### II.4 Resistance Measurement

A four-terminal 0.1 ohm standard resistor whose temperature was monitored throughout the course of the experiment was connected in series with the specimens. A constant current of 10 or 20 milliamperes was maintained and self-heating was not noticeable for these currents. Potentials were measured with a Type 9160 Potentiometer and Type 5214/9460 Photo-cell Galvanometer Amplifier (manufactured by Guildline Instruments Ltd.) in conjunction with a Pye Scalamp Galvanometer. To eliminate thermal emfs in the leads, the potential was alternately measured for the standard resistor and the unknown resistance with normal and



reversed currents and the average of the two values of the unknown resistance was thus determined. Guildline thermal-free switches were used for potential selection and current reversal.

Since the potentiometer was linear to within 20 parts per million and since the voltage null detection system could detect a change of  $10^{-8}$  volts, it was possible to determine relative resistance to within  $\pm 0.005\%$  or  $1\ \mu\text{-ohm}$  whichever was greater. The standard resistor was calibrated to an accuracy of  $\pm 0.0005\%$  by comparing it with a precision variable resistor.

The current and the potential leads to the specimens consisted of very fine (0.0045 inch diameter) copper wires with four layers of Formel insulation. They were thermally anchored at  $t$  in the cryostat. The thermal anchoring was done by wrapping several turns of the wires around the pumping tube. These leads after emerging from the tube  $P_2$  terminated on copper binding posts attached to a thick copper plate. The end of the tube  $P_2$  was sealed with black wax. Stranded copper wires were used for connecting the binding posts on the cryostat to the potentiometer.



## II. 5 Specimen Preparation

(a) Preliminary. Aluminum used in the preparation of alloys was supplied by Aluminum Company of Canada, Ltd. (ALCAN), and magnesium was obtained from Johnson, Matthey and Co. Ltd.

The purity of these metals was as follows:

Aluminum (ALCAN) - 99.996 % pure

Magnesium - Matthey spectrographically standardized  
Mg with impurities less than 14 parts  
per million.

(b) Preparation of the pure Al wire. A bar of Al 6 mm x 11 mm x 80 mm was cut from the Al block. To remove surface contamination, it was etched in hot concentrated potassium hydroxide and then with concentrated nitric acid, thoroughly rinsed with distilled water and dried. This Al bar was melted in a horizontal boat of high-grade graphite placed in a resistance-wound furnace described by Rogers (1962). The graphite boat, before being used, was outgassed at 1000°C in vacuum. The furnace tube surrounding the specimen was evacuated and flushed twice with helium to remove air. An activated coconut charcoal trap placed in liquid nitrogen (White, 1959) was used to clean the helium. The melting was done in vacuum ( $\sim 10^{-4}$  mm pressure) at 700°C.





The Al rod thus obtained was drawn through steel rollers to reduce its cross-section and then through steel dies to obtain a wire of about 1.5 mm diameter. This wire was cleaned with a strong solution of KOH and then with  $\text{HNO}_3$  to remove any iron picked up in rolling and drawing. The thick Al wire was then drawn through diamond dies until its diameter was reduced to about 0.9 mm. The wire was again cleaned and then further drawn through diamond dies to give a 1/2 mm diameter wire.

This wire was loosely wound on a 4/5 inch diameter Pyrex glass tube and rinsed with acetone and dried. It was annealed at  $400^\circ\text{C}$  for 24 hours in vacuum ( $\sim 10^{-5}$  mm pressure). The furnace tube was flushed twice with helium before annealing. The annealed wire gave the resistance ratio  $R(293) / R(4.2) \simeq 660$ .

(c) Preparation of alloys. The alloys were prepared using the radio-frequency (R.F.) induction furnace in the Department of Mining and Metallurgy. Before being used, Mg was etched with 1 % hydrochloric acid and rinsed with distilled water. It was further rinsed with 1 % potassium dichromate solution to prevent oxidation (Das and Gerritsen, 1962), then rinsed with distilled water and quickly dried. Weighed quantities of Al and Mg, about 12 grams of charge for each alloy, were



melted in alundum (RA 84) crucibles in a helium atmosphere. Alumina crucibles could not be used as Al reacts with alumina. Graphite crucibles cannot be used in an induction furnace in order to make a good alloy, so alundum was chosen (Whittaker, 1958). The average frequency of the induction furnace during specimen preparation was  $\sim 1000$  kc/sec. Sufficient time was given for Mg to dissolve in Al to form a homogeneous alloy. Since Mg has a high vapour pressure near its melting point, evaporation was prevented by introducing pieces of Mg into a hole drilled in a small block of Al. The hole was closed with an Al plug. Judging from the amount of Mg deposited around the edge of the crucible, very little loss of Mg by evaporation was noticed. The alloy ingots thus obtained were scraped and etched strongly to remove alundum from the surface touching the crucible. They were then examined under a microscope to look for traces of alundum on the surface.

(d) Remelting of alloys. In order to obtain alloys in the form of a rod so that wires could be drawn easily, the ingots were remelted in a high-grade graphite crucible (Figure 4). This crucible was kept vertical in the coil of the induction furnace in a helium atmosphere. A section of the upper part of the rod obtained in this way was cut and set aside for metallographic examination.





Figure 4

The Graphite Crucible





(e) Homogenization of alloys. The alloys were placed in a graphite boat and homogenized at  $500^{\circ}\text{C}$  for 24 hours in vacuum. A small section of each homogeneous alloy was cut for metallographic examination. Figure 5 shows (a) the unhomogenized and (b) the homogenized Al + 2 at. % Mg alloy under 75X magnification. Before and after homogenization both the alloys were weighed and a reduction  $\sim 0.005\%$  in weight was observed.

All alundum crucibles, the graphite crucible and boat used in the preparation of the alloys were outgassed at  $1000^{\circ}\text{C}$  in vacuum before being used.

(f) Preparation of alloy wires. The surface layer of each alloy rod was removed by filing and then etching. The rods were drawn to 0.5 mm diameter wires in exactly the same manner as described for the pure Al specimen. The two alloy wires were annealed separately at  $400^{\circ}\text{C}$  for 24 hours in vacuum. The resistance ratio  $R(293)/R(4.2)$  for the two specimens is given below.

$$\text{Al} + 2 \text{ at. \% Mg alloy} \quad -- \quad \frac{R(293)}{R(4.2)} \quad \simeq \quad 12.5$$

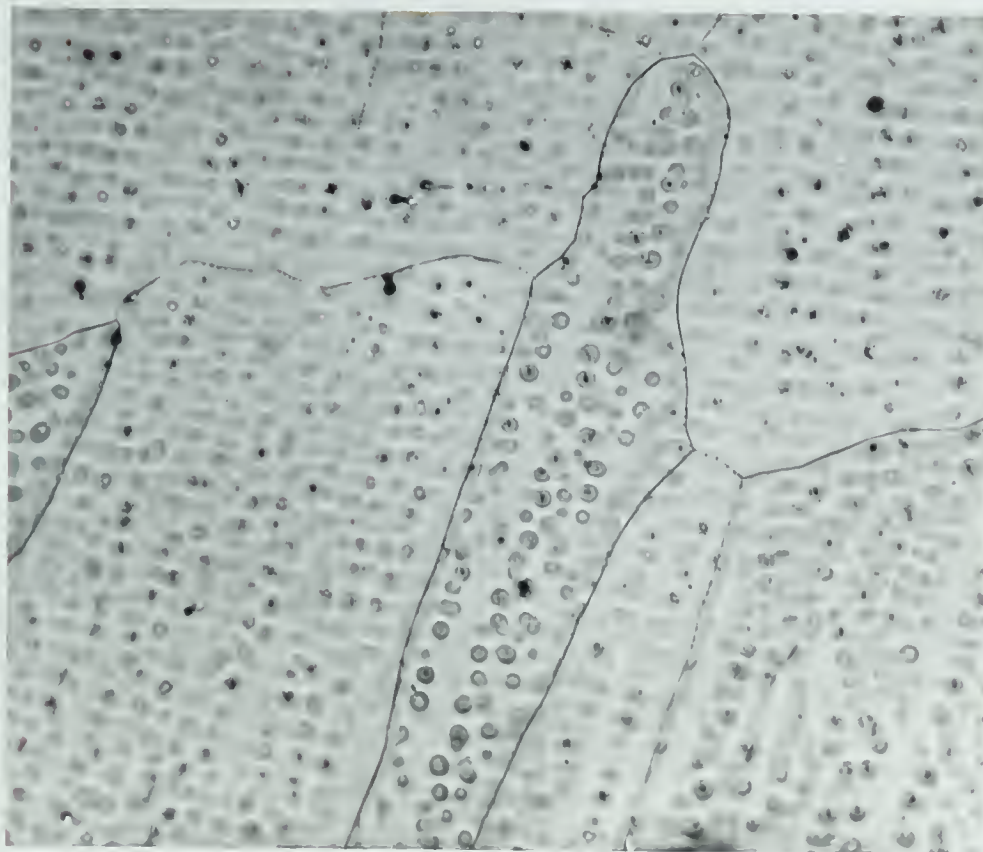
$$\text{Al} + 1.5 \text{ at. \% Mg alloy} \quad -- \quad \frac{R(293)}{R(4.2)} \quad \simeq \quad 22.5$$



Figure 5

Photomicrographs of (a) the unhomogenized Al + 2 at. % Mg alloy showing coring in as cast, and (b) the homogenized Al + 2 at. % Mg alloy.





(a)



(b)





## II.6 Experimental Procedure

(a) Uniformity and homogeneity of the wires. As indicated in II.1, the geometrical factors should be known accurately and were determined by weighing a measured length of wire. The mass in conjunction with the length and density of a wire determined a mean value of its area of cross-section over the length of the wire. The measured resistance of a wire on the other hand depends on the mean of the reciprocal of the cross-section along the length of the wire, and the reciprocal of one mean value is not necessarily equal to the other mean value. In order to estimate the magnitude of the discrepancy between these two values, the resistance per 10 cm of length was measured along the whole length of the wire.

In order to measure the resistance per unit length accurately, a travelling potential probe was designed. It consists of a flat lucite bar, over 100 cm long on which was milled a straight groove 0.022 inch wide and 0.015 inch deep. The specimen wire could lie smoothly in this groove. A potential probe (Figure 6) in which the potential contacts were provided by two stretched fine wires about 10 cm apart, moves over the wire under study. A constant current was maintained through the wire and the potential was measured across each 10 cm length along the wire. The distance between the potential contacts was read by a cathetometer capable of



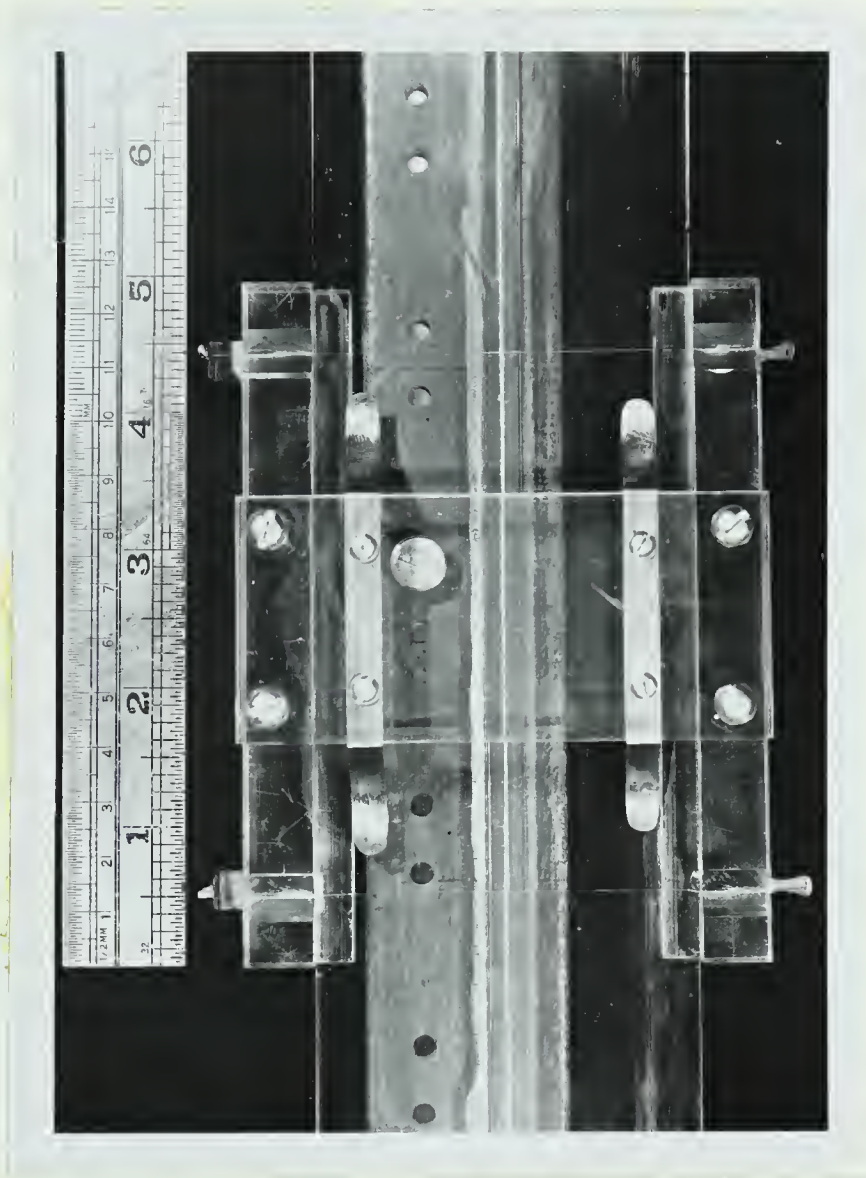


Figure 6

The Potential Probe



reading 0.01 mm. Within the range of experimental error, the resistance per unit length  $R/l$  along the pure Al wire was found to have a standard deviation from the average of 0.07 %. For the alloy wire, assuming a constant diameter the homogeneity was checked. The standard deviation of  $R/l$  from the average in this case was again  $\sim 0.07$  %. According to the analysis given in Appendix II, these deviations are sufficiently small that no appreciable error is introduced in assuming the wires to be uniform and homogeneous.

(b) Length of the specimens. With a sharp edge, marks were put near the ends of the wire and the distance between them measured with a cathetometer. The potential clips of the specimen holder were placed over these marks.

After the resistance measurements in the cryostat, each wire was uncoiled from the specimen holder and its length again measured in order to study the effect of bending on the length of the wire. For 100 cm long samples, an increase of 1 mm for pure Al wires and 0.5 mm for the alloy wires was observed. This small change in length was the major source of error in the measurement of the geometrical factor  $l/A$ .





(c) Variation of specimen resistance with thermal cycling. It was noticed that the ice-point resistivity of the annealed alloy samples increased by about 0.4 % after they had been thermally cycled once to 80°K or lower. While this effect was small, it had a pronounced effect on  $\Delta\rho$  at temperatures above 80°K. It was found, however, that further thermal cycling caused no appreciable shift in  $\Delta\rho$ . This effect is not uncommon (White, 1959). It is not clear why the effect is not commulative with additional thermal cycling. Since it was not, all samples were thermally cycled twice between room-temperature and 80°K prior to making detailed resistance measurements. The samples were left for 12 hours at each end-point temperature of each cycle.

(d) Resistance measurements of the specimens. The resistances of the pure Al wire and the alloy wire were measured together at the same temperature. First the resistance readings were taken at room-temperature and at 78°K using liquid nitrogen. The cryostat was then cooled to 4.2°K and the residual resistance of each wire measured. No attempt was made to cool the specimens below 4.2°K as it is known (Aleksandrov and D'yakov, 1963) that there is no appreciable decrease in resistance of Al below 4.2°K. Using the liquid helium bath, temperature was raised by 5 to 10 degree steps and readings were taken up to 45°K. After the helium run, the resistance measurements were repeated at 78°K.



A liquid oxygen bath was used to obtain a measurement at 90°K and this observation was repeated after taking the last set of readings at room-temperature.

(e)  $\ell/A$  measurements. After the complete run, the specimens were removed from the cryostat and their lengths measured. Their ends were cut at the fixed marks and masses determined by weighing on a microbalance. In terms of mass  $m$ , length  $\ell$ , and density  $d$ ,  $\frac{\ell}{A} = \frac{\ell^2 d}{m}$ . The density of pure Al and each alloy was calculated from the mass and concentration of the solute atoms and the lattice parameters (Pearson, 1958) of Al and the alloys.



## PART III

### RESULTS

#### III.1 Analysis of Results

The resistance-temperature data for the specimens were collected over a period of eight weeks of continuous cryostat operation. The resistance data were converted to resistivity data by using the room-temperature values for the geometrical factors. The effect of thermal expansion on  $\frac{\ell}{A}$  was ignored. Even if this is taken into account, it has little effect on the  $\Delta\rho$  values calculated here.

The definition of  $\Delta\rho(T)$  given earlier was

$$\Delta\rho(T) = \rho(T) - \rho_i(T) - \rho_o, \quad (1)$$

where 
$$\rho_o = \lim_{T \rightarrow 0} \rho(T), \quad (2)$$

and 
$$\rho_i(T) = \lim_{\rho_o \rightarrow 0} \rho(T). \quad (3)$$

If we designate the pure and the alloy samples by subscripts P and A respectively, then an excellent approximation for (2) is

$$\rho_o = \rho(0) = \rho(4.2^\circ\text{K}).$$





An approximation for (3) which only causes about 2% error in  $\Delta\rho$  for the alloys measured is (Berry, 1963)

$$\rho_i(T) = \rho_P(T) - \rho_P(0) \quad . \quad (4)$$

In (4) the departure from Matthiessen's rule is ignored and this is permissible provided  $\rho_P(0) \ll \rho_A(0)$  . Thus relation (1) becomes,

$$\Delta\rho(T) = \rho_A(T) - \rho_P(T) - [\rho_A(4.2^\circ\text{K}) - \rho_P(4.2^\circ\text{K})] \quad . \quad (5)$$

The results giving the ideal resistivity of aluminum, the alloy resistivity and the corresponding deviations from Matthiessen's rule for the two alloys are shown in Tables 1 and 2. Graphs of  $\Delta\rho$  vs.  $T$  and  $\rho_i$  vs.  $T$  are shown in Figures 7, 8 and 9. The room-temperature values of the ideal resistivity are accurate to  $\pm 0.21\%$ , the major source of error being the uncertainty in the measurement of  $\ell/A$ . At low temperatures, the uncertainty in the resistance measurements was at the most  $\pm 0.5\%$ .

Considering only the errors in the measurement of resistance, the resulting error in  $\Delta\rho$  is of the order of  $8.5 \times 10^{-11}$  ohm-cm. Any error in the measurement of the geometrical factor  $f = \frac{\ell}{A}$  appears as an error in  $\Delta\rho$  proportional to  $\rho_i$ . If the error in  $f_A$ , for an alloy, is  $df_A$  and



and the corresponding quantities for the pure specimen are  $f_P$  and  $d f_P$ , it can be shown (Alley and Serin, 1959) that the absolute value of the fractional error introduced into the calculation of  $\Delta\rho$  is

$$\left| \frac{d(\Delta\rho)}{\Delta\rho} \right| = \left| \frac{d f_A}{f_A} \right| + \frac{\rho_i}{\Delta\rho} \left[ \left| \frac{d f_A}{f_A} \right| + \left| \frac{d f_P}{f_P} \right| \right].$$

Since at high temperatures,  $\rho_i \gg \Delta\rho$ , the error introduced in  $\Delta\rho$  can indeed be very large.

### III.2 Discussion of Results and Conclusions

Figure 8 shows the variation of the deviations from Matthiessen's rule with temperature. The deviations are positive throughout the temperature range considered and are larger than expected. Some typical values of the quantity  $(\frac{\Delta\rho}{\rho_A - \Delta\rho}) \times 100$  at various temperatures are shown in Table 3. This quantity shows a maximum for both the alloys in the temperature interval, 50°K to 60°K. For the 2 % alloy,  $\rho_i \simeq \rho_0$  near 80°K and for the 1.5 % alloy,  $\rho_i \simeq \rho_0$  near 65°K. The ideal resistivity of Al at low temperatures varies as  $T$  to the power  $(3.7 \pm 0.1)$ .



Tables of Experimental Results

Table 1

Al and Al + 2 at. % Mg alloy

$$\rho_P(4.2^\circ\text{K}) = 4.075 \times 10^{-9} \text{ ohm-cm } (\pm 0.71 \%)$$

$$\rho_A(4.2^\circ\text{K}) = 2.3681 \times 10^{-7} \text{ ohm-cm } (\pm 0.12 \%)$$

$$\left. \frac{\ell}{A} \right)_P = 48754.9 \text{ cm}^{-1} (\pm 0.21 \%) \text{ at } 20^\circ\text{C}$$

$$\left. \frac{\ell}{A} \right)_A = 48294.5 \text{ cm}^{-1} (\pm 0.11 \%) \text{ at } 20^\circ\text{C}$$

$T(^{\circ}\text{K})$	$\rho_{\text{ideal}}$ ohm-cm	$\rho_{\text{Alloy}}$ ohm-cm	$\Delta\rho$ ohm-cm
10.2	$0.254 \times 10^{-9}$	$2.3726 \times 10^{-7}$	$0.020 \times 10^{-8}$
16.1	$1.008 \times 10^{-9}$	$2.3854 \times 10^{-7}$	$0.072 \times 10^{-8}$
21.3	$2.397 \times 10^{-9}$	$2.4128 \times 10^{-7}$	$0.207 \times 10^{-8}$
27.3	$5.676 \times 10^{-9}$	$2.4748 \times 10^{-7}$	$0.499 \times 10^{-8}$
31.5	$1.001 \times 10^{-8}$	$2.5467 \times 10^{-7}$	$0.785 \times 10^{-8}$
61.0	$1.0514 \times 10^{-7}$	$3.6762 \times 10^{-7}$	$2.567 \times 10^{-8}$
64.8	$1.2899 \times 10^{-7}$	$3.9239 \times 10^{-7}$	$2.659 \times 10^{-8}$
70.0	$1.6538 \times 10^{-7}$	$4.2994 \times 10^{-7}$	$2.775 \times 10^{-8}$





Table 1 (cont.)

$T(^{\circ}\text{K})$	$\rho_{\text{ideal}}$ ohm-cm	$\rho_{\text{Alloy}}$ ohm-cm	$\Delta\rho$ ohm-cm
76.76	$2.1800 \times 10^{-7}$	$4.8431 \times 10^{-7}$	$2.950 \times 10^{-8}$
76.76	$2.1832 \times 10^{-7}$	$4.8459 \times 10^{-7}$	$2.946 \times 10^{-8}$
89.51	$3.3753 \times 10^{-7}$	$6.0563 \times 10^{-7}$	$3.129 \times 10^{-8}$
89.51	$3.3752 \times 10^{-7}$	$6.0559 \times 10^{-7}$	$3.126 \times 10^{-8}$
138	$8.5749 \times 10^{-7}$	$1.12755 \times 10^{-6}$	$3.325 \times 10^{-8}$
193.7	$1.52811 \times 10^{-6}$	$1.80535 \times 10^{-6}$	$4.043 \times 10^{-8}$
237	$2.03775 \times 10^{-6}$	$2.31872 \times 10^{-6}$	$4.416 \times 10^{-8}$
273.15	$2.44332 \times 10^{-6}$	$2.73119 \times 10^{-6}$	$5.106 \times 10^{-8}$
293.25	$2.67511 \times 10^{-6}$	$2.96406 \times 10^{-6}$	$5.214 \times 10^{-8}$



Table 2

Al and Al + 1.5 at. % Mg alloy

$$\rho_P(4.2^\circ\text{K}) = 4.398 \times 10^{-9} \text{ ohm-cm } (\pm 0.66\%)$$

$$\rho_A(4.2^\circ\text{K}) = 1.2570 \times 10^{-7} \text{ ohm-cm } (\pm 0.12\%)$$

$$\left. \frac{\ell}{A} \right)_P = 48699.7 \text{ cm}^{-1} (\pm 0.21\%) \text{ at } 20^\circ\text{C}$$

$$\left. \frac{\ell}{A} \right)_A = 48202.1 \text{ cm}^{-1} (\pm 0.11\%) \text{ at } 20^\circ\text{C}$$

$T(^{\circ}\text{K})$	$\rho_{\text{ideal}}$ ohm-cm	$\rho_{\text{Alloy}}$ ohm-cm	$\Delta\rho$ ohm-cm
9.9	$0.208 \times 10^{-9}$	$1.2595 \times 10^{-7}$	$0.004 \times 10^{-8}$
18.6	$1.346 \times 10^{-9}$	$1.2785 \times 10^{-7}$	$0.080 \times 10^{-8}$
31.2	$0.761 \times 10^{-8}$	$1.3866 \times 10^{-7}$	$0.535 \times 10^{-8}$
47.0	$3.807 \times 10^{-8}$	$1.7750 \times 10^{-7}$	$1.373 \times 10^{-8}$
64.0	$1.2260 \times 10^{-7}$	$2.6694 \times 10^{-7}$	$1.864 \times 10^{-8}$
64.0	$1.2258 \times 10^{-7}$	$2.6693 \times 10^{-7}$	$1.865 \times 10^{-8}$
76.75	$2.1938 \times 10^{-7}$	$3.6409 \times 10^{-7}$	$1.901 \times 10^{-8}$
76.75	$2.1937 \times 10^{-7}$	$3.6410 \times 10^{-7}$	$1.903 \times 10^{-8}$
76.78	$2.1962 \times 10^{-7}$	$3.6435 \times 10^{-7}$	$1.903 \times 10^{-8}$
76.78	$2.1980 \times 10^{-7}$	$3.6453 \times 10^{-7}$	$1.903 \times 10^{-8}$



Table 2 (cont.)

T(°K)	$\rho_{\text{ideal}}$ ohm-cm	$\rho_{\text{Alloy}}$ ohm-cm	$\Delta\rho$ ohm-cm
89.54	$3.3734 \times 10^{-7}$	$4.8153 \times 10^{-7}$	$1.849 \times 10^{-8}$
89.54	$3.3733 \times 10^{-7}$	$4.8149 \times 10^{-7}$	$1.846 \times 10^{-8}$
89.48	$3.3631 \times 10^{-7}$	$4.8041 \times 10^{-7}$	$1.840 \times 10^{-8}$
89.48	$3.3648 \times 10^{-7}$	$4.8055 \times 10^{-7}$	$1.837 \times 10^{-8}$
138	$8.4625 \times 10^{-7}$	$9.8887 \times 10^{-7}$	$1.692 \times 10^{-8}$
139	$8.5090 \times 10^{-7}$	$9.9348 \times 10^{-7}$	$1.688 \times 10^{-8}$
193.6	$1.52354 \times 10^{-6}$	$1.66695 \times 10^{-6}$	$1.771 \times 10^{-8}$
213	$1.77146 \times 10^{-6}$	$1.91583 \times 10^{-6}$	$1.867 \times 10^{-8}$
213	$1.77042 \times 10^{-6}$	$1.91475 \times 10^{-6}$	$1.863 \times 10^{-8}$
237	$2.04242 \times 10^{-6}$	$2.18801 \times 10^{-6}$	$1.989 \times 10^{-8}$
237	$2.04207 \times 10^{-6}$	$2.18756 \times 10^{-6}$	$1.979 \times 10^{-8}$
245	$2.14050 \times 10^{-6}$	$2.28659 \times 10^{-6}$	$2.039 \times 10^{-8}$
245	$2.14144 \times 10^{-6}$	$2.28761 \times 10^{-6}$	$2.047 \times 10^{-8}$
273.15	$2.43802 \times 10^{-6}$	$2.58575 \times 10^{-6}$	$2.203 \times 10^{-8}$
273.15	$2.43815 \times 10^{-6}$	$2.58572 \times 10^{-6}$	$2.187 \times 10^{-8}$
293.15	$2.66591 \times 10^{-6}$	$2.81553 \times 10^{-6}$	$2.392 \times 10^{-8}$
293.25	$2.66737 \times 10^{-6}$	$2.81723 \times 10^{-6}$	$2.416 \times 10^{-8}$
293.25	$2.66722 \times 10^{-6}$	$2.81704 \times 10^{-6}$	$2.412 \times 10^{-8}$





Figure 7

Graph of  $\Delta\rho$  vs.  $T$  for Al + 2 at. % Mg and Al + 1.5 at. % Mg alloys. The dotted curves correspond to the systematic error due to uncertainty in the  $l/A$  ratios.



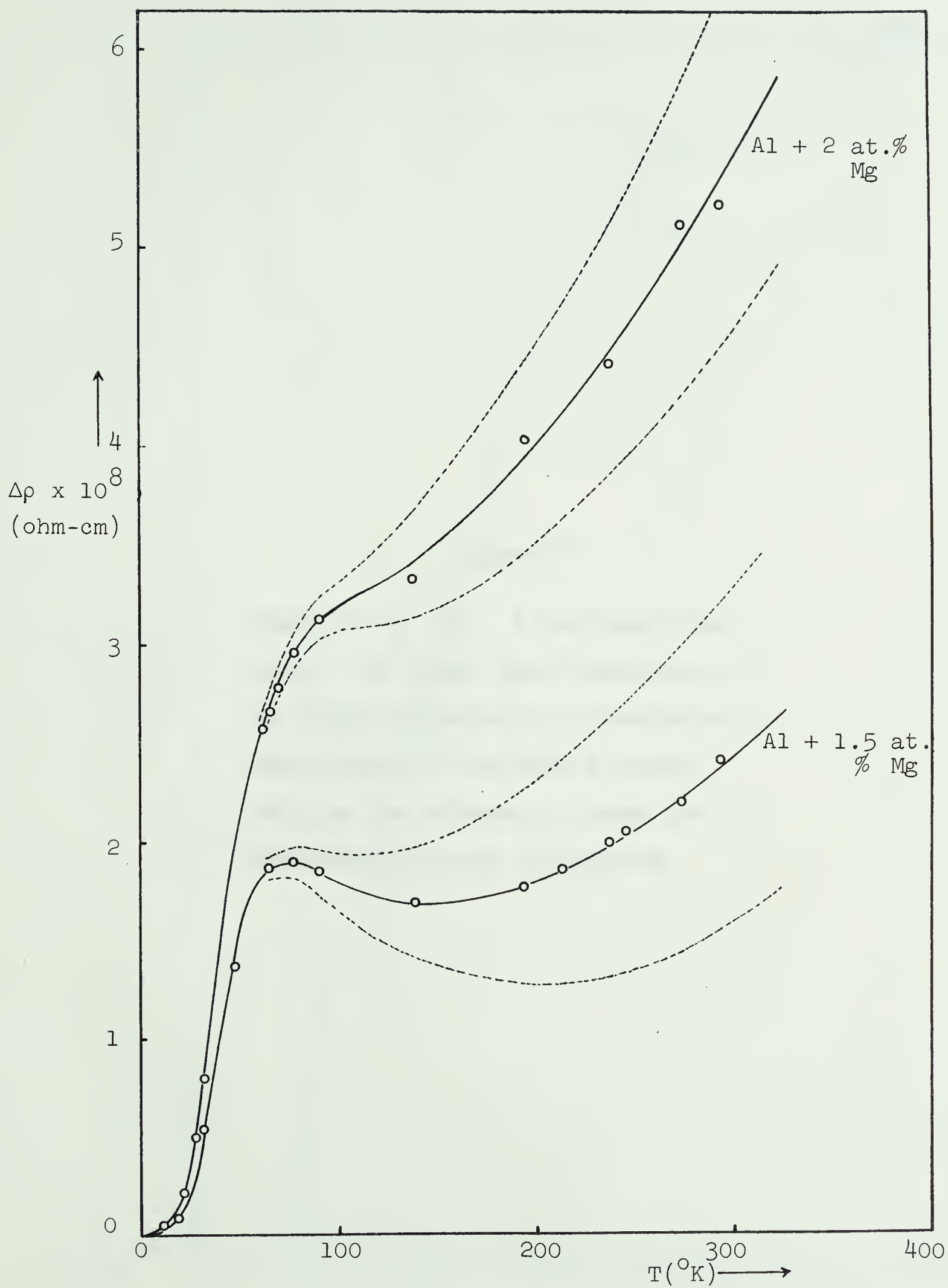




Figure 8

Graph of  $\Delta\rho$  vs.  $T$  on logarithmic scale. The error bars correspond to the random uncertainty in resistance measurements. The dotted curves indicate the systematic error due to uncertainty in the  $\ell/A$  ratios.





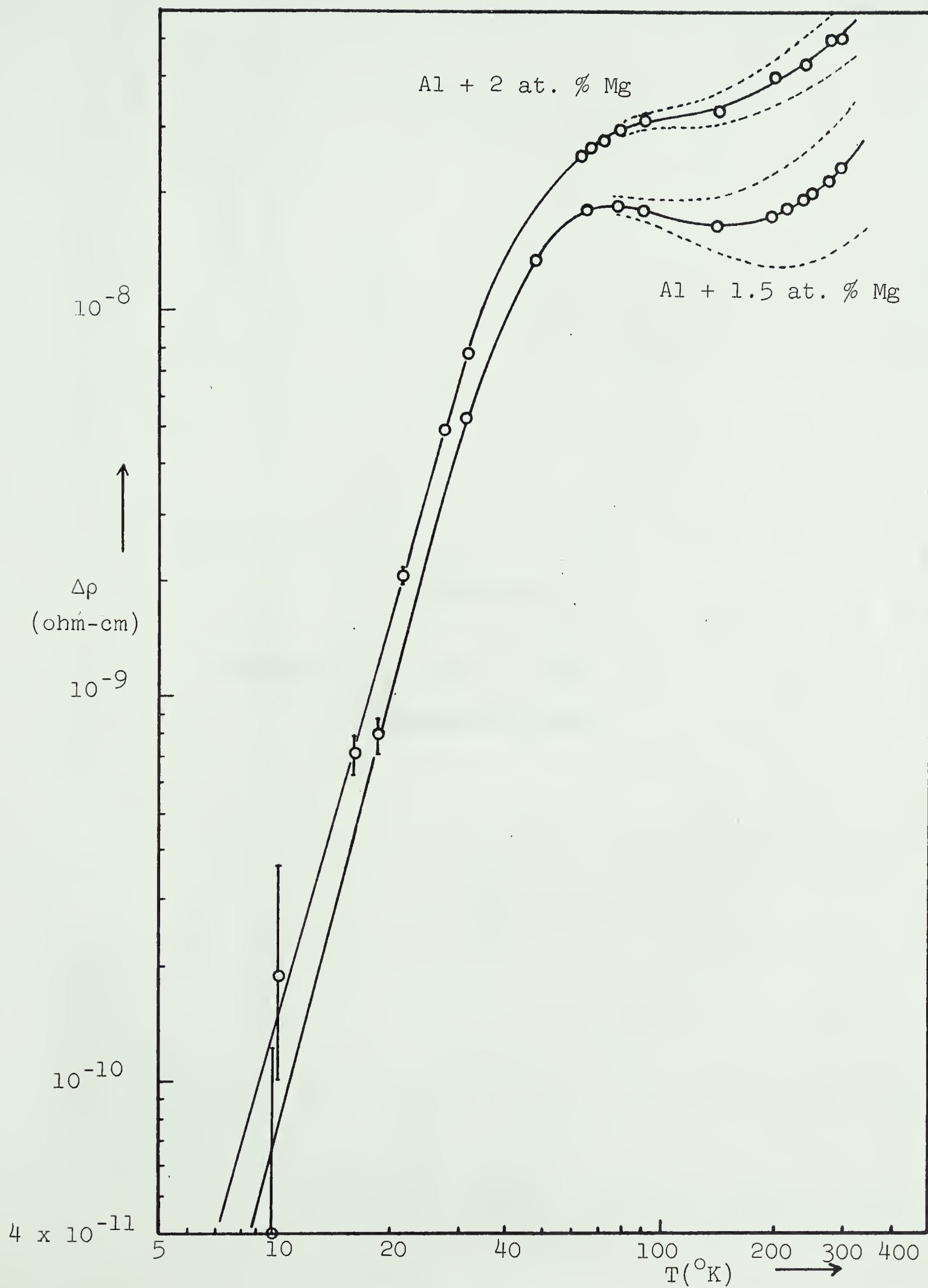




Figure 9

Graph of  $\rho_i$  vs.  $T$  for Al on  
logarithmic scale.



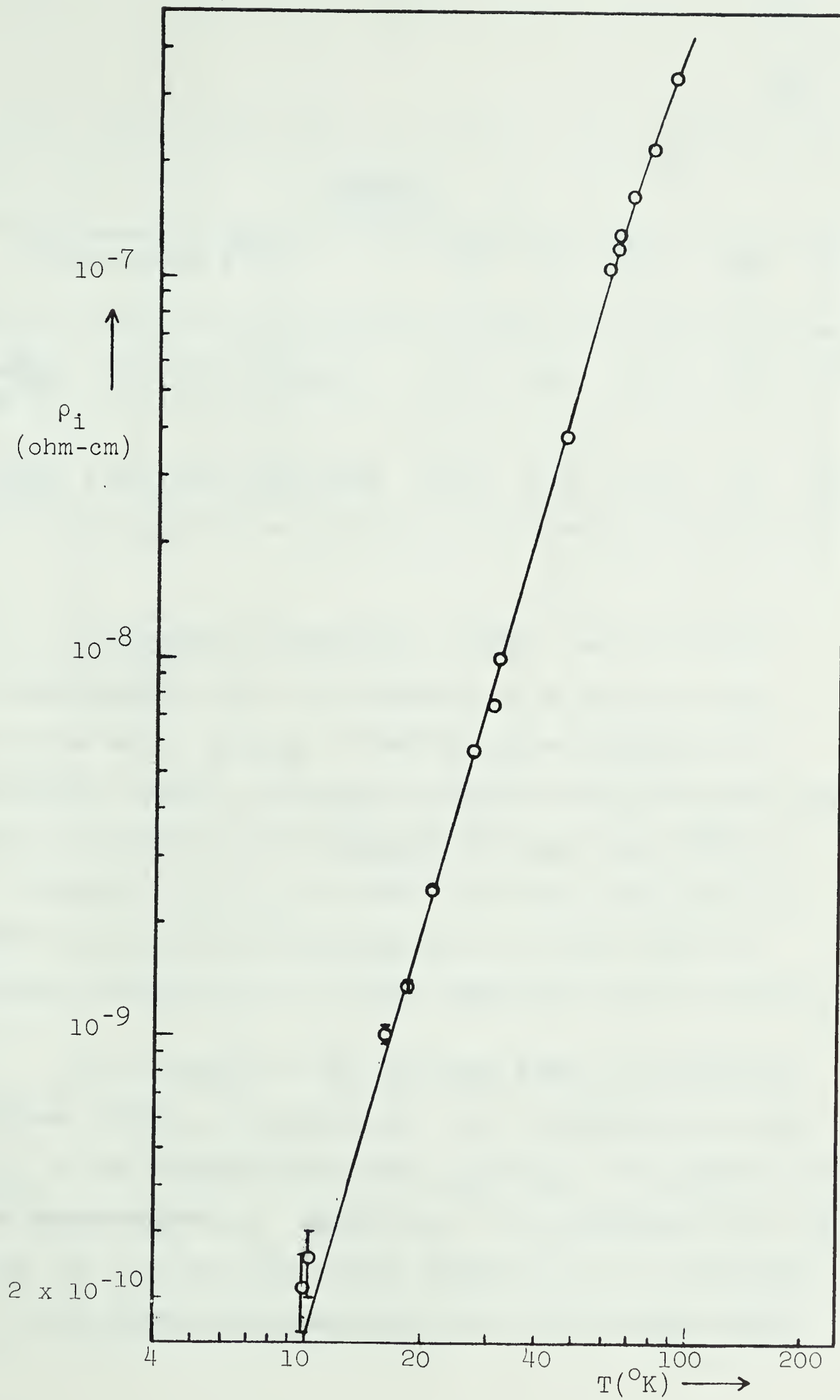






Table 3

Temperature ( $^{\circ}\text{K}$ )	31	77	90	194	273
$(\frac{\Delta\rho}{\rho_A - \Delta\rho}) \times 100$ for 2% alloy	3.2	6.5	5.4	2.3	1.9
$(\frac{\Delta\rho}{\rho_A - \Delta\rho}) \times 100$ for 1.5% alloy	4.0	5.5	4.0	1.1	0.9

According to Sondheimer (1950), the deviations from Matthiessen's rule are expected to be positive and significant when  $\rho_i \simeq \rho_o$ . From the above analysis of experimental results, we observe that the deviations for both alloys are maximum in the temperature range from  $50^{\circ}\text{K}$  to  $60^{\circ}\text{K}$ . However,  $\rho_i \simeq \rho_o$  at  $65^{\circ}\text{K}$  for the 1.5% alloy and at  $80^{\circ}\text{K}$  for the 2% alloy showing that in both cases the deviations are maximum at a lower temperature than expected.

On the basis of the two-band model of Sondheimer and Wilson (1947), the deviations  $\Delta\rho$  are expected to vary as  $\rho_i$  at low temperatures where  $\rho_o \gg \rho_i$ . We observe that at low temperatures,  $\rho_i$  varies as  $T$  to the power  $(3.7 \pm 0.1)$  whereas  $\Delta\rho$  for both the alloys varies as  $T$  to the power  $(3.5 \pm 0.5)$  showing some agreement with the two-band model.



At higher temperatures where  $\rho_i \gg \rho_o$ ,  $\Delta\rho$  is expected to become constant and proportional to  $\rho_o$  which is not the case for the two alloys we investigated.

It cannot be said for certain if the variation of  $\Delta\rho$  with  $T$  to the power  $(3.5 \pm 0.5)$  in the low-temperature range can be attributed to the strain at the impurity site in the lattice as suggested by Klemens (1963). The contribution to impurity resistivity due to strain has been shown to lead to deviations from Matthiessen's rule proportional to  $T^4$ , but this is just one of many other causes contributing to the deviations.

We now discuss our results on the basis of Kagan and Zhernov's (1966) theory. In doing so, we shall also consider the results of Hedgcock and Muir (1964) on alloys of Mg with Al impurity. The deviations from Matthiessen's rule for Mg + 2.41 at. % Al alloy are shown in Figure 10. For Mg-Al alloys,  $S > 0$  and therefore the impurity resistivity is expected to increase monotonically with temperature in the low-temperature region. But as shown by Hedgcock and Muir (1964), the impurity resistivity first decreases and then increases with temperature; it passes through a maximum at about 70°K before decreasing almost linearly with temperature. For Al-Mg alloys,  $S < 0$ . The impurity resistivity is expected to pass through a maximum given by



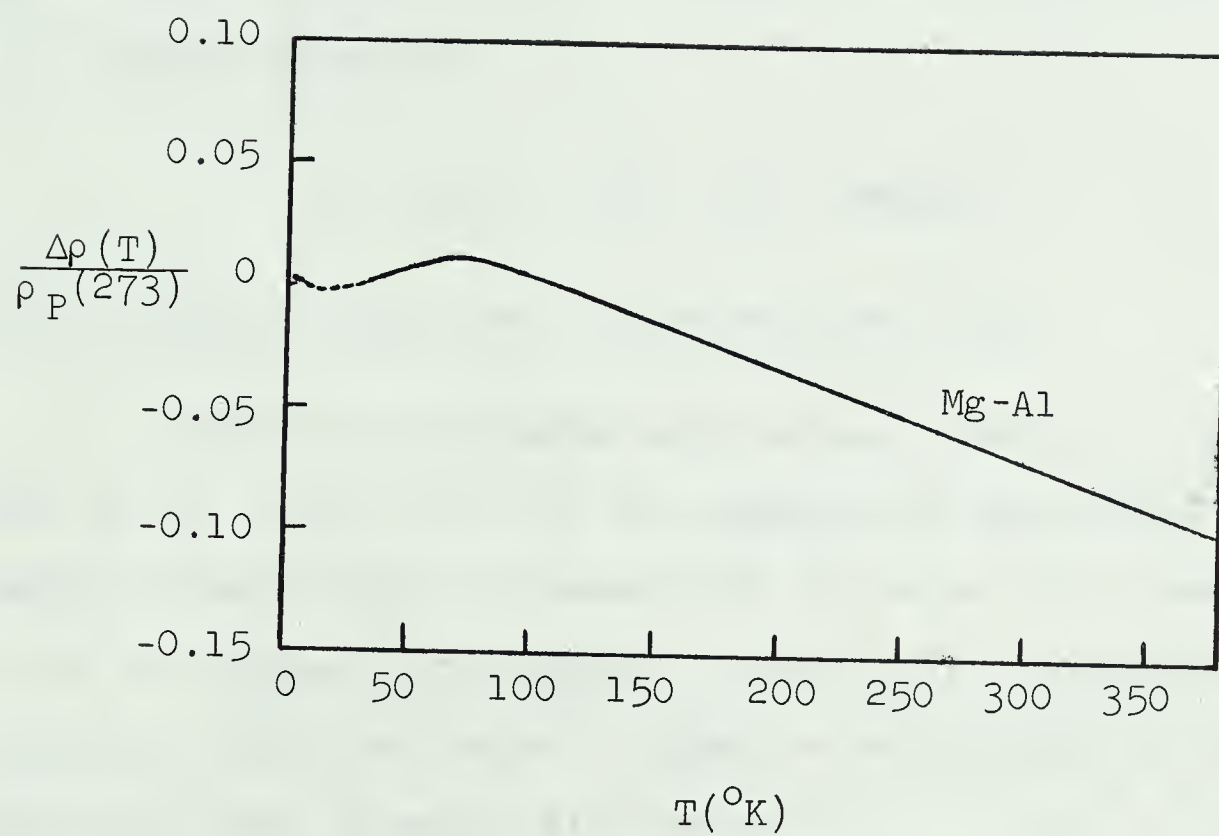


Figure 10

Deviations from Matthiessen's Rule for

Mg + 2.41 at. % Al Alloy

[Hedgcock and Muir (1964)]





$$(\text{Impurity Resistivity})_{T_{\max}} = 3C (-S)(\rho_{\text{ideal}})_{T_{\max}} .$$

For the Al + 1.5 at. % Mg alloy,  $T_{\max} \simeq 77^{\circ}\text{K}$  ;  $S \simeq -\frac{4}{9}$  and  $\rho_{\text{ideal}} \simeq 2.2 \times 10^{-7}$  ohm-cm. The impurity resistivity should therefore be approximately equal to  $4.4 \times 10^{-9}$  ohm-cm. But the experimental value of impurity resistivity for Al + 1.5% Mg alloy is

$$\rho_A - \rho_P \simeq 1.41 \times 10^{-7} \text{ ohm-cm} ,$$

which is much larger than the calculated value.

According to Kagan and Zhernov (1966), in the limit when  $q \rightarrow 0$  and  $(Z' - Z)$  is negative (Al-Mg alloys), the impurity resistivity is expected to increase with temperature in the low-temperature region. In the high-temperature region, the above condition leads to negative deviations  $\Delta\rho$  which should decrease linearly with temperature. Thus  $\Delta\rho$  as a function of temperature should pass through a maximum, then through zero at a certain temperature retaining a negative sign at high temperatures. This behaviour is shown by Mg-Al alloys rather than by Al-Mg alloys. For the case when  $(Z' - Z) > 0$  (Mg-Al alloys), in the limit of small  $q$ ,  $\Delta\rho$  is expected to have positive sign both at low and high temperatures. In the intermediate temperature region, the curve may be quite



complicated with one or more inflection points and even with loss of monotonicity in some cases. A linear increase of impurity resistivity with temperature is common to all the cases in the theory for the region of high temperatures. It is clear that this behaviour is not shown by Mg-Al alloys but to some extent, it is shown by Al-Mg alloys. Kagan and Zhernov point out that their theory cannot explain the behaviour of Mg alloys with Al impurity. In fact the observed behaviour of Mg-Al alloys corresponds to the theoretical prediction for Al-Mg alloys and vice-versa. Whether this is the consequence of the specific nature of the pseudopotentials for large  $q$  or whether the initial premises of the theory are violated for this pair of metals cannot be readily decided. Perhaps, the first possibility is more likely.

Kagan and Zhernov (1966) have also pointed out that at high temperatures, a simple relation holds approximately between the sign of the slope of  $\Delta\rho$  vs.  $T$  curve and the relative positions in the periodic table of the two metals in the alloy. In other words, for alloys in which the solute and the solvent atoms exchange roles, a reversal of slope of  $\Delta\rho$  vs.  $T$  curves is expected at high temperatures. Our present study together with the work of Hedgcock and Muir (1964) show that this is valid for the Al-Mg system.



In conclusion, we may add that the available experimental data on deviations from Matthiessen's rule are inadequate to confirm or deny the predictions of the Kagan and Zhernov's theory. Extensive studies of the impurity resistivity of alloys over a wide temperature range and for different solute concentrations are necessary to permit a more comprehensive check of the theory.



## Appendix 1

### Reversal of Slope of $\Delta\rho$ vs. $T$ Curves for a Complementary Alloy System<sup>\*</sup>

We can show qualitatively by a simple argument the reversal of slope of  $\Delta\rho$  vs.  $T$  curves for a complementary pair of alloys. Suppose that there is a fraction  $c$  of  $A$  atoms and  $(1-c)$  of  $B$  atoms; also suppose that the effective (pseudo) potentials around these atoms are  $V_A(\vec{r})$  and  $V_B(\vec{r})$  respectively. For qualitative argument we further assume that  $V_A(\vec{r})$  and  $V_B(\vec{r})$  are independent of  $c$ .

The probability  $P_{\vec{k}\vec{k}'}$ , that an electron at  $\vec{r}$  is scattered from state  $\vec{k}$  to state  $\vec{k}'$  is proportional to

$$\left| \langle \vec{k}' | \sum_{A,B} V_{A,B}(\vec{r} - \vec{R}_{A,B}) | \vec{k} \rangle \right|^2, \quad (1)$$

where  $\vec{R}_A$  and  $\vec{R}_B$  denote the positions occupied by  $A$  and  $B$  atoms. Relation (1) can be written (in Born approximation) as

$$P_{\vec{k}\vec{k}'} \equiv P(\vec{K}) \propto \sum_{i,j} U_i(\vec{K}) U_j(\vec{K}) e^{i\vec{K} \cdot (\vec{R}_j - \vec{R}_i)} \quad (2)$$

where the summation is over all the lattice sites and

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<sup>\*</sup> The author is grateful to Professor A.B. Bhatia for the discussion presented in this appendix.





$$\vec{K} = \vec{k} - \vec{k}' = 2 k \sin \frac{\theta}{2} .$$

$U_i(\vec{K})$  is the Fourier transform of  $V_A(\vec{r})$  or  $V_B(\vec{r})$  [i.e.,

$$U_A(\vec{K}) \propto \int e^{i\vec{K} \cdot \vec{r}} V_A(\vec{r}) d\vec{r} ,$$

and similarly  $U_B(\vec{K})$ ] according as the atom  $i$  is A or B. The bar in (2) represents the statistical average.  $U_A$  and  $U_B$  are real since  $V_A$  and  $V_B$  are real.

If the alloy is random, then for  $i \neq j$  ,

$$\begin{aligned} \overline{U_i U_j} &= \overline{U_i} \overline{U_j} = (\overline{U})^2 \\ &= [c U_A + (1 - c) U_B]^2 , \end{aligned}$$

and for  $i = j$  ,

$$\overline{U_i^2} = \overline{U^2} = c U_A^2 + (1 - c) U_B^2 .$$

With these results,

$$\overline{U_i U_j} = (\overline{U})^2 + \delta_{ij} [\overline{U^2} - (\overline{U})^2] . \quad (3)$$

Substituting (3) in (2), we get

$$P(\vec{K}) \propto (\overline{U})^2 \left| \sum_i e^{i\vec{K} \cdot \vec{R}_i} \right|^2 + N[\overline{U^2} - (\overline{U})^2] , \quad (4)$$

where  $N$  = total number of atoms.



In (4), the first term gives the temperature-dependent part of the resistivity and at higher temperatures,

$$\left| \sum_i e^{i\vec{K} \cdot \vec{R}_i} \right|^2 \propto T \quad (\text{Sham and Ziman, 1963}).$$

The second term in (4) is the residual resistivity.

For qualitative purposes, we may assume that  $U_A(\vec{K})$  and  $U_B(\vec{K})$  are independent of the angle of scattering  $\theta$ . This would be true if the electron wavelength was large compared to the interatomic distance. Then the resistivity  $\rho$  would be proportional to  $P(K)$  and hence

$$\rho = \alpha [c U_A + (1 - c)U_B]^2 T + \beta c (1 - c)[U_B - U_A]^2, \quad (5)$$

$\alpha$  and  $\beta$  being constants. The first term in this expression is the temperature-dependent resistivity of the alloy and the second term is the residual resistivity. Since  $c$  is small, we retain only the terms linear in  $c$  and write

$$\rho = \alpha [U_B^2 + 2c (U_A - U_B)U_B] T + \beta c (U_B - U_A)^2. \quad (6)$$

The deviation from Matthiessen's rule has been defined as

$$\Delta\rho = \rho_A - \rho_i - \rho_o.$$



Therefore,

$$\Delta\rho \text{ (Solvent metal B)} = \alpha U_B (U_A - U_B) 2c T, \quad (7)$$

where

$$\rho_i(B) = \alpha U_B^2 T.$$

Similarly, if we have a concentration  $c$  of metal B in metal A, then

$$\Delta\rho \text{ (Solvent metal A)} = \alpha U_A (U_B - U_A) 2c T. \quad (8)$$

It is clear from equations (7) and (8) that interchanging the metals in an alloy would interchange the slope of the  $\Delta\rho$  vs.  $T$  curve.





## Appendix II

### Uniformity and Homogeneity of Wires

#### 1. Uniformity of Cross-sectional Area of Wires.

The resistance of a wire of length  $\ell$  and cross-sectional area  $A$  is given by

$$R = \rho \frac{\ell}{A} . \quad (1)$$

Small variations in cross-sectional area may be taken into account by writing

$$A = A(\ell) = A_0 [1 + \alpha(\ell)] . \quad (2)$$

If  $A_0$  is taken to be the mean cross-sectional area as determined by weighing, it follows that

$$\int_0^L \alpha(\ell) d\ell = 0 , \quad (3)$$

where  $L$  is the total length of the wire. The expression for resistance then becomes

$$R = \frac{\rho}{A_0} \int_0^L [1 + \alpha(\ell)]^{-1} d\ell ,$$

or

$$R \simeq \frac{\rho}{A_0} \int_0^L [1 + [\alpha(\ell)]^2] d\ell . \quad (4)$$



Since the correction term  $[\alpha(l)]^2$  is of second order,  $\alpha(l)$  itself need only be determined to a modest precision relative to  $\frac{l}{A}$ .

It is possible to estimate the magnitude of  $\alpha(l)$  by measuring the resistance per unit length over successive 10 cm intervals. Let  $R_n$  be the resistance of a 10 cm interval  $l_n$ , it follows that

$$\frac{R_n}{l_n} \approx \left. \frac{dR}{dl} \right|_n \approx \frac{\rho}{A_0} [1 - \alpha(l_n)] ,$$

or

$$\frac{R_n}{l_n} = \left\langle \frac{R_n}{l_n} \right\rangle_{av.} [1 - \alpha(l_n)] . \quad (5)$$

The values  $\frac{R_n}{l_n}$  are therefore a measure of the quantity  $\alpha(l_n)$  provided  $\alpha(l)$  does not vary rapidly over the interval  $l_n$ . Experimentally,  $\alpha(l_n)$  never exceeded  $\pm 0.1\%$ . Furthermore, no short-period ripples in the diameter of the wire were observed under a microscope. The correction term  $[\alpha(l)]^2$  in equation (4) was accordingly deemed negligible for our purpose.



## 2. Homogeneity of the Alloy Wires.

The mean deviation of the values  $\frac{R_n}{l_n}$  for the alloy wires was only slightly larger than that for the pure wires, so that the alloy wires were homogeneous to 0.1 % or better. This amount of inhomogeneity is easily tolerated since  $\Delta\rho$  is roughly proportional to the impurity concentration.



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